Chapter 16
Advanced Oxidation Processes

16-1. General

Advanced Oxidation Processes (AOP) and their applications are described in the chapter's first section. The second portion of the chapter is a hazard analysis with controls and control points listed.

16-2. Technology Description

a. Process.

Advanced oxidation processes are destructive treatments that oxidize organic and explosive constituents in wastewater either photochemically or by direct oxidation through the addition of strong oxidizers, or a combination of the two. The photolytic oxidation reactions are achieved through the synergistic action of UV light, in combination with ozone (O_3) or hydrogen peroxide (H_2O_2) or other catalysts and reagents. Lamps that generate UV light shine on the flow path for the water stream, and the ozone or peroxide, or both, are injected upstream of the lamps. If complete mineralization is achieved, the final products of the oxidation are carbon dioxide, water, and salts. AOPs can use a combination of hydrogen peroxide, ozone, and peroxide catalyzed oxidation, or UV lights in combination with hydrogen peroxide alone, ozone alone, or a combination of hydrogen peroxide and ozone together to treat the aqueous stream.

The main advantage of AOPs is that they are destructive processes, as opposed to air stripping or carbon absorption, in which contaminants are extracted and concentrated in a separate phase. The oxidation process can be configured in batch or continuous flow modes, depending on the required flow and concentrations. See Figure 16-1.

b. Applications.

The process is effective only for relatively clear aqueous streams. Turbidity in the water will prevent UV light, if used, from fully penetrating the water stream.

For additional information on similar processes, see Chapter 18.

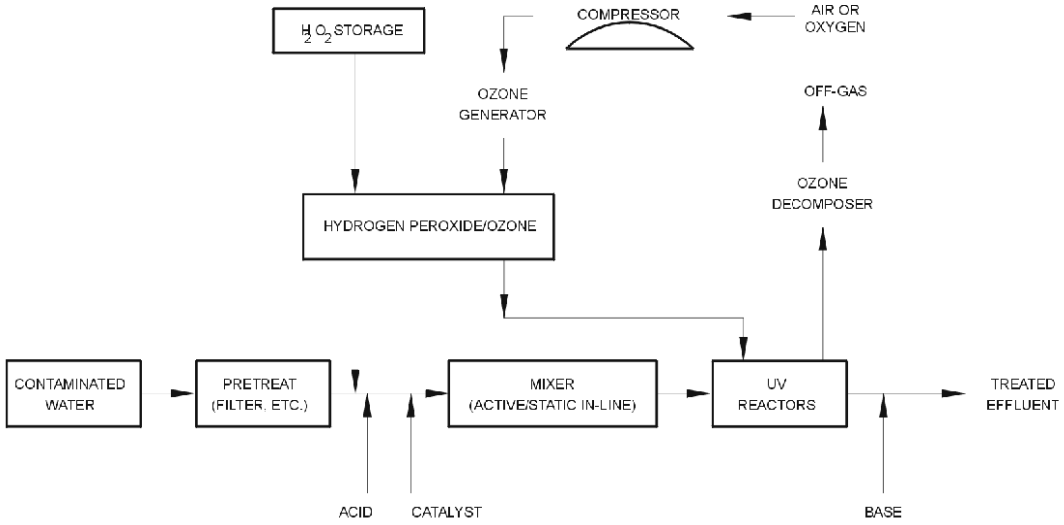

FIGURE 16-1. TYPICAL PROCESS FLOW FOR ULTRAVIOLET OXIDATION

16-3. Hazard Analysis

Principal unique hazards associated with advanced oxidation processes, methods for control, and control points are described below.

a. Physical Hazards.

(1) *Heated Surfaces.*
Description. Certain components of UV type AOP treatment systems, such as the UV lamps' protective sheaths, the ozone generator, and the ozone off-gas destruction units, can generate heated surfaces that may cause burns to unprotected skin or create radiant heat hazards.

Control. Controls for heated surfaces include:
- Insulate or cool surfaces either by ventilation or through a heat exchanger.
- Wear insulated gloves to prevent thermal burns.
- Minimize worker exposure time on or near hot surfaces.
- If prolonged work is required near radiant heat sources, use appropriate eye and body protection.

CONTROL POINT: Design, Operations, Maintenance

(2) *Electrocution.*
Description. UV oxidation systems utilize high-voltage mercury lamps that may operate on voltages up to 3000 volts. Breakage of the lamps may cause electrocution or mercury vapor (see paragraph 16-3*b*(1) of this Chapter).

Control: Controls for electrocution include:

- Verify that drawings indicate the hazardous area classifications as defined in National Fire Protection Association (NFPA) 70, Chapter 5, sections 500.1 through 500.10.
- Use controls, wiring, and equipment that meet the requirements of EM 385-1-1, Section 11, and NFPA 70 for the identified hazard areas.
- Perform all electrical work according to code and under the supervision of a state licensed master electrician.
- Use grounded or ground fault interrupter circuit (GFIC)-protected equipment if required by EM 385-1-1, Section 11, or NFPA 70 (special grounding requirements).
- Verify UV lamp cover panel interlocks de-energize the system when doors are opened.

CONTROL POINT: Design, Construction, Operations, Maintenance

(3) *Explosion and Combustion Hazards.*

Description. Although hydrogen peroxide solutions (27–52%) are not combustible, as strong oxidizers they can greatly intensify combustion. They also present an explosion hazard because of violent decomposition when heated or contaminated with oxidizable materials including iron, copper, brass, bronze, copper, and other metals (see Material Safety Data Sheets for complete listing). Contact with reducing agents or organic and combustible materials (wood, paper) may cause immediate spontaneous ignition.

Control. Controls for explosion include:

- Implement a plant-specific lock-out/tag-out program designed after the requirements of 29 CFR 1910.147 for maintenance procedures.
- Perform a Process Hazard Analysis (PHA) prior to startup and correct all deficiencies found.
- Implement a plant-specific hazard communication program for plant operators on the reactive properties of hydrogen peroxide. Design in compliance with the requirements of 29 CFR 1910.1200.
- Store hydrogen peroxide solutions in properly vented, approved containers in a cool, clean, fire-resistant area away from combustible materials, catalytic metals, direct sunlight, and other potential sources of heat or ignition.
- Maintain the purity of the solution.
- Do not return unused material to its storage container after removal.
- Select, design, and maintain all equipment in contact with hydrogen peroxide solutions to minimize reactive hazards.
- Use secondary containment in storage areas.
- Supply an ample source of water for handling spills.
- Train the operators in emergency procedures in case of a catastrophic failure, in life saving first aid procedures including halting the thermal reac-

tions, extracting, extinguishing, decontaminating and stabilizing victims, and in emergency system isolation and shutdown procedures.

- Locate emergency fire fighting equipment, eyewashes and showers at critical points throughout the system. (See American National Standards Institute ANSI Z358.1 – 1998.)

CONTROL POINT: Design, Operations, Maintenance

(4) *Confined Spaces*.

Description. Workers may be exposed to confined space hazards when entering an AOP facility's treatment vaults and vessels that require entry as a normal part of inspection, operation, and maintenance. The units such as the hydrogen peroxide storage unit, the hydrogen peroxide/ozone combining chamber, or the mixing tank, can be operated under oxygen deficient or poisonous atmospheric conditions. All treatment units requiring periodic entry for maintenance present significant confined space hazards. Death or injury can be caused by inhalation in the oxygen deficient or poisonous atmosphere, or also by engulfment hazards

Control. Controls for confined spaces include:

- Eliminate confined space in the design where possible (designers). If confined spaces cannot be eliminated, design the process vaults, tanks, and vessels to maximize easy operation, and physical cleaning and maintenance to include accessible, adequately sized access doors and ports, and to minimize the frequency, duration, and extent of cleaning and maintenance required. Designs should minimize maintenance required in the spaces.
- Ensure that liquid oxygen storage vessels and distribution systems comply with the requirements, including labeling, specified in NFPA 50 and 29 CFR 1910.104 (designers).
- Implement and follow a plant-specific confined-space entry program designed after the requirements of the Occupational Safety and Health Administration's (OSHA's) confined-space standard in 29 CFR 1910.146.
- Test the atmospheres within the confined spaces prior to entry and monitor throughout the work being performed. (See 29 CFR 1910.146.)
- Design air ventilation to minimize or eliminate oxygen-deficient or poisonous gas pockets and rigorously ventilate prior to entry of personnel.
- Perform manufacturers shutdown procedures and lockout/tag out of electrically energized systems prior to entry.
- Use air-supplied respirators to control inhalation exposures to poisonous atmospheres and prevent any potential for asphyxiation in situations where only constant mechanical ventilation prevents the buildup of a toxic or inert gas environment.
- Implement a plant-specific hazard communication program for plant operators on the hazardous properties of liquid oxygen. Design in compliance with the requirements of 29 CFR 1910.1200.

CONTROL POINT: Design, Operations, Maintenance

(5) *Explosion and Fire Hazards*.

Description. Operation of AOP systems can generate gases and build pressure in the process units. There is a hazard for the workers for an explosion and release of the reagents and contaminated materials. Some UV/oxidation systems use liquid oxygen to generate ozone. Liquid oxygen storage creates the potential for fire and explosion.

Control. Controls for explosion and fire include:

- Include pressure-relief valves and vents discharged away from the work area (designers).
- Perform a Process Hazard Analysis (PHA) prior to startup and correct all deficiencies found.
- Consider including alarm systems, monitors to detect pressure build-up and ozone, emergency release systems for head spaces, and emergency plans for operations.
- Train workers in hazards associated with all potential gases generated, including ozone odor detection.
- Train the operators in emergency procedures in the event of a catastrophic failure, in life saving first aid procedures including halting the thermal reactions, extracting, extinguishing, decontaminating and stabilizing victims, and in emergency system isolation and shutdown procedures.
- Locate emergency fire fighting equipment, eyewashes and showers at critical points throughout the system. (See ANSI Z358.1 – 1998.)

CONTROL POINT: Design, Operations, Maintenance

(6) *Treatment Buildings*.

Description. Permanent or semi-permanent treatment buildings may present life safety hazards such as inadequate egress, fire suppression systems, or emergency lighting systems.

Control. Controls for treatment buildings include:

- Meet the following construction requirements for permanent and semi-permanent treatment system buildings: ANSI 58.1, “Minimum Design Loads for Buildings and Other Structures,” the “National Fire Code,” the “National Standard Plumbing Code,” “Life Safety Code,” and the “Uniform Building Code.”
- Make sure structures comply with either the Air Force Manuals on Air Force bases, the USACE Technical Manuals on Army installations, or local building codes on Superfund, Base Realignment and Closure (BRAC) or Formerly Used Defense Sites (FUDS) sites.

CONTROL POINT: Design, Operations

(7) *UV Radiation*.

Description. The operation of a UV-based treatment system utilizes lamps that emit UV radiation that may cause eye damage.

Control. Controls for UV radiation include:

- Wear the appropriate ANSI-approved eye protection, utilizing the appropriate shade.
- Verify that interlocks are functional.
- Verify that view ports properly filter UV rays.
- Verify that UV lamp sheaths are not cracked or broken.

CONTROL POINT: Operations, Maintenance

(8) *Noise hazards.*

Description. Noise hazards may be associated with the use of an air compressor to generate ozone.

Control. Controls for noise hazards include:

- Include isolated generator rooms in building design.
- Develop a hearing protection policy in accordance with 29 CFR 1910.95.

CONTROL POINT: Design, Operations, Maintenance

(9) *Emergency Wash Equipment.*

Description. Emergency shower/eyewash equipment required per 19 CFR 1910.151 is not always provided with adequate floor drains, thereby creating potential electrical hazards or walking surface hazards during required testing and use.

Control. A control for emergency wash equipment includes:

- See American National Standards Institute ANSI Z 358.1 – 1998: "Emergency Eyewash and Shower Equipment" for design requirements.
- Equip showers/eyewash equipment with accompanying functional drains to isolate and collect the shower/eyewash water from unprotected electrical equipment and walking surfaces that, when wet, create slipping hazards.

CONTROL POINT: Design

(10) *Design Field Activities.*

Description. Design field activities associated with subsequent construction may include surveying, biological surveys, soil gas surveys, geophysical surveys, trenching, drilling, stockpiling, contaminated groundwater sampling, and other activities. Each of these field activities may expose the survey personnel to physical, chemical, radiological, and biological hazards.

Control. Controls for hazards resulting from design field activities include:

- Prepare an activity hazard analysis for design field survey activities. EM 385-1-1, Section 1, provides guidance on developing an activity hazard analysis.
- Train workers in hazards identified.

CONTROL POINT: Design

b. Chemical Hazards.

(1) *Toxic Material Exposure (Feed or Byproducts).*
Description. During operation of the AOP units, workers may be exposed to toxic components in the waste water, the toxic chemical additives, reagents or catalysts in the chemical storage units, the chemical feed and mixing tanks and in the reaction vessels; to oxygen deficient atmospheres and carbon dioxide; or to airborne poisons including hydrogen peroxide or ozone vapors or gas, catalysts, heavy metals such as mercury (e.g., broken mercury vapor lamps) or metal salts. Bulk chemical additives can create exposure potentials, both when the chemicals are replenished and when routine maintenance is done on the treatment units.

Control. Controls for exposure to toxic materials include:
- Train all workers involved in both the operation and maintenance of the AOPs and in all chemical hazards related to the generation, transport, and treatment of the contaminants, contaminant byproducts within the system, and the bulk chemical additives used to treat the contaminants.
- Characterize and classify the gaseous waste components prior to and following oxidation.
- Feed only liquid waste streams compatible with the process into the unit.
- Note design parameters on feed characteristics.
- Design chemical treatment technologies appropriate for the known or anticipated wastes.
- Design engineering controls for the system to prevent or minimize the generation or release of toxic materials/gases into the breathing zone of the workers, both during operation and maintenance. The engineering controls could include real time monitors with alarms and appropriate ventilation controls.
- Install, locate, and maintain emergency eyewash and shower units at critical points throughout the system. (See ANSI Z358.1 – 1998.)
- Use personal protective equipment (PPE) appropriate to the work task, to the contaminants to be treated, and to the oxidation byproducts, such as chemical protective gear, acid protective gear, chemical safety goggles, safety glasses, face shields, air-supplied respirators, etc. Train workers in the use of the PPE.

CONTROL POINT: Design, Operations

(2) *Mercury*.

Description. Workers may be exposed to mercury if mercury vapor-filled lamps are damaged or broken during installation, inspection, or replacement. Mercury overexposure may cause various symptoms, including damage to the central nervous system, conjunctivitis, and inflammation to the nose and throat.

Control. Controls for mercury include:

- Handle mercury lamps with caution to help prevent breakage.
- Remove mercury spills immediately.
- Make mercury spill kits available in the immediate work areas.

CONTROL POINT: Construction, Operations, Maintenance

(3) *Ozone*.

Description. Ozone may be produced via an on-site ozonator to enhance the performance of UV oxidation systems. Ozone may leak through seals or pipe junctions, or ozone levels may increase in the work environment if the ozonator fouls. Ozone is a potential experimental tumorigen and teratogen. Exposure to ozone may irritate exposed skin. Depending upon the degree of exposure, ozone may cause irritation of the eyes and respiratory tract, diminished lung function, painful or difficulty breathing, chest tightness, coughing, wheezing, increased sensitivity of the lungs to allergens and bronchoconstrictors, and increased susceptibility to lung-based bacterial and viral infections.

Control. Controls for ozone include:

- Use local or general ventilation of the work area. Observe wind direction, and proximity of wind to fresh air inlets.
- Use closed tops and controlled vents on the reaction chambers.
- Use gas-tight covers or active ventilation on sumps and holding tanks downstream of ozone generation systems.
- Vent vessels (passively or actively) through ozone decomposition equipment to the outside of the building.
- Interlock equipment with ozone generation equipment.
- Set equipment to shut ozone generation off if plant levels exceed the ACGIH TLV for ozone.
- Install real time monitors and alarm systems to warn plant operators if plant levels exceed the ACGIH TLV for the type of work performed by them , i.e., light, moderate, or heavy.
- Implement a plant-specific hazard communication program to identify and address the signs and symptoms of ozone exposure, including odor identification, and to provide procedures for reducing exposures.

CONTROL POINT: Design, Operations, Maintenance

(4) *Catalysts*.

Description. Worker inhalation/ingestion/dermal exposure may occur during the use of catalysts in conjunction with UV oxidation.

Control. Controls for catalysts include:

- Minimize all contact with catalysts. Adhere to the manufacturer's handling instructions and the recommendations of the MSDS for the catalyst.
- Wear personal protective equipment (PPE) and clothing such as an air-purifying respirator with N, R or P100 or N, R or P95 filters, chemically inert disposable coveralls, and protective gloves (e.g., nitrile) based on the materials to be handled.

CONTROL POINT: Design, Operations, Maintenance

(5) *Hydrogen Peroxide*.

Description. Hydrogen peroxide may also be used to help improve the efficiency of UV oxidation systems. Hydrogen peroxide is an oxidizer that may react violently with organic materials either in the waste stream or in other materials, causing fire or system over-pressurization. Exposure to hydrogen peroxide may cause irritation or chemical burns to the skin and damage eyes. Dermal or eye contact with or inhalation of hydrogen peroxide mists or solutions pose a hazard to personnel from chemical burns associated with acute exposure.

Control. Controls for hydrogen peroxide include:

- Provide secondary containment for storage of hydrogen peroxide.
- Use PPE when solution handling is required. Gloves made of natural rubber or nitrile offer good chemical resistance to solutions of 30–70% hydrogen peroxide. Leather and many fabrics, including cotton, rayon, and wool, should not be worn when handling hydrogen peroxide solutions because they present a fire hazard if spills occur. Instead, wear polyester-acrylic (anti-static treated) garments.
- Wear splash-proof chemical safety goggles and face-shields.
- Use local ventilation or respiratory protection to control mists as determined by a qualified health and safety professional.
- Train workers in hydrogen peroxide hazard identification/control.

CONTROL POINT: Design, Operations, Maintenance

(6) *Acids and Bases*.

Description. Workers may be exposed to pH control agents (acids and bases) during operations.

Control. Controls for acids and bases include:

- Construct secondary containment storage areas for acids and bases and use compatible storage materials.
- Mark storage containers clearly.
- Store acids and bases in separate areas.
- Locate emergency showers and eye wash stations that comply with 29 CFR 1910.151(c) and ANSI Z358.1 - 1998 near the reagent storage areas.

- Automate handling of pH agents to the extent practical.
- Prepare an emergency plan and train facility personnel to safely handle acids and bases.
- Restrict manual handling of acids and bases to personnel familiar with their properties. Follow the guidelines of the MSDS.
- Use PPE such as leather or rubber acid-resistant boots, chemical-resistant coveralls, goggles and face shields, air-purifying respirators (as indicated by the reagent), and rubber or other acid and base resistant gloves (e.g., nitrile) or gauntlets.
- Train workers in safe acid/base handling techniques.

CONTROL POINT: Design, Operations, Maintenance

c. Radiological Hazards.

(1) *UV Radiation.*
Description. The mercury lamps used in the treatment generate high levels of UV radiation. Typically, the UV is contained within the treatment unit. However, radiation that is released may damage eyes or increase the risk of skin cancer.

Control. Controls for UV radiation include:
- Equip the reactor vessel with interlocks that de-energize the system when the door is opened.
- Equip viewing ports in reactor walls with glass covers that prevent transmission of UV radiation.

CONTROL POINT: Design, Operations, Maintenance

(2) *Radioactive Devices*
Description. Fire and smoke detection devices, fluid level devices, and other process monitors and switches may contain radioactive devices potentially exposing workers through lack of identification or mishandling.

Control. Controls for inadvertent handling or exposure to radioactive devices include:
- Workers should be prevented from and warned against tampering with the devices.
- The location of the devices should be recorded so as to safely retrieve and dispose of them in case of a system failure and equipment replacement.

CONTROL POINT: Design, Operations and Maintenance

d. Biological Hazards.

Opportunistic Insects and Animals.

Description. For all sites but especially in cooler climates, opportunistic insects or animals can nest in and around warm process equipment. Vermin, insect, and arthropod control measures should be considered in any design.

Control. Control of opportunistic insect and animals include:

- Electrical cabinets and other infrequently opened enclosures should be opened carefully and checked for black widow and brown recluse spiders, and evidence of rodents. As rodents can cause damage to electrical cables, all wiring should be inspected regularly.
- Ensure all storage is off the ground, palleted, and kept dry. Damp areas attract scorpions, rodents, and the snakes that eat them.
- Design ceiling corners and other high areas to discourage nesting by swallows, pigeons, and other birds. Birds are carriers of diseases, especially in their droppings, which can foul cranes and process equipment.

CONTROL POINT: Design, Operations and Maintenance